J Chem Crystallogr (2008) 38:295–299
DOI 10.1007/s10870-007-9306-6

ORIGINAL PAPER

X-ray Diffraction and DFT Studies of 2-Methoxy-5-phenylaniline

Ana T. Marques · Joana A. Silva · Manuela Ramos Silva · Ana Matos Beja · Licinia L. G. Justino · Abilio J. F. N. Sobral

Received: 31 August 2007 / Accepted: 5 November 2007 / Published online: 27 November 2007

Abstract 2-Methoxy-5-phenylaniline, a promissor monomer for PANI studies, has been characterized by single-crystal X-ray diffraction at two temperatures: orthorhombic, space group $P2_12_12_1$, $Z = 12$ with $a = 5.9900(2)$ Å, $b = 20.4873(6)$ Å, $c = 26.3727(8)$ Å and $R = 0.0868$ for 293(2) K and $a = 5.8337(9)$ Å, $b = 20.4428(31)$ Å, $c = 26.0773(40)$ Å and $R = 0.0669$ for 120(2) K. There are three independent molecules in the unit cell. One of them is approximately planar, the other two have the phenyl rings rotated. At room temperature the two latter molecules are joined in dimers through H-bonds and at low temperature the same molecules are joined in columns that run along the *a*-axis.

Keywords Polyaniline · Polymer · Biphenyl

Introduction

Polyanilines (PANIs) can be synthesized from monomeric anilines either by chemical or electrochemical oxidative polymerization, as a bulk powder or film [1, 2]. PANIs are one of the more extensively studied conductive polymers due to its high electrical performance and easy conductivity control, thermal stability, easy handling and inexpensive synthesis [2–4]. It has been shown that functionalization of the polymer backbone alters the ion exchange properties of the polymer making it suitable to be used in pH sensor/actuators and as material for battery applications [3–5]. 2-Methoxy-5-phenylaniline is a compound that combines the aniline motifs with the biphenyl characteristics being a promissor monomer for PANI studies. Preliminary results on the polymerization of 2-methoxy-5-phenylaniline show the formation of oligomeric chains with more than six monomers per chain.

Many theoretical studies have been done on the class of conducting conjugated polymers, namely on their building blocks like biphenyl, trying to elucidate their optical and transport properties [6–9]. The former studies have shown that the crystalline molecular conformation of biphenyl is very different from that exhibited by the isolated molecule as seen by the different torsion angles between rings.

A. T. Marques · J. A. Silva · L. L. G. Justino · A. J. F. N. Sobral
Chemistry Department, University of Coimbra,
3004-535 Coimbra, Portugal

M. R. Silva (✉) · A. M. Beja
CEMDRX, Physics Department, University of Coimbra,
3004-516 Coimbra, Portugal
e-mail: manuela@pollux.fis.uc.pt

Experimental and Computational Methods

2-Methoxy-5-phenylaniline was purchased from Aldrich and was used as received. Dichloromethane was purified as described elsewhere [10]. All others analytical reagents were purchased from commercial sources and used without further purification.

Crystal Structure Determination

A crystal of the title compound with needle shape and having approximate dimensions of 0.44 mm × 0.05 mm × 0.02 mm was glued on a glass fiber and mounted on a Bruker Apex II diffractometer. Diffraction data were collected at room temperature 293(2) K and low temperature 120(2) K using graphite monochromated Mo $K\alpha$ ($\lambda = 0.71073$ Å).

Data were processed using PLATON and an absorption correction (using SADABS) was applied which resulted in transmission factors ranging from 0.970 to 0.998 [11, 12]. Data were corrected for Lorentz and Polarization effects. Reflections with $2\theta \leq 55°$ were used for structure solution and refinement.

The structure was solved by direct methods using SHELXS-97 [13]. It was refined by full-matrix least-squares on F^2 using the SHELXL-97 program [13]. All the hydrogen atoms were placed at calculated positions and allowed to ride on their parent atoms using SHELXL-97 defaults. At room temperature, one of the independent molecules showed some disorder and its atoms were refined isotropically, all other atoms (non-H) were refined anisotropically. Due to the lack of anomalous dispersion at the Mo*K*a wavelength, Friedel pairs were merged. The final least-squares cycle was based on 2,308 observed reflections [$I > 2\sigma(I)$] and 334 variable parameters, converged with $R = 0.0868$ and $wR = 0.2982$ for room temperature. For low temperature, the refinement converged with $R = 0.0669$ and $wR = 0.1812$ based on 2,106 observed reflections [$I > 2\sigma(I)$] and 409 variable parameters. Crystallographic details, selected interatomic distances and angles and geometric details of H-bonds are given in Tables 1–3, respectively.

DFT Studies

DFT structure optimization of the dimer was performed using the code GAMESS [14], starting from the X-ray geometry. The calculations employed the B3LYP (Becke three-parameter Lee–Yang–Parr) exchange correlation functional, which combines the hybrid exchange functional of Becke [15, 16] with the correlation functional of Lee, Yang and Parr [17]. The 631++*G*(*d*,*p*) basis sets were used for the expansion of the Kohn–Sham orbitals [18–21]. At the final equilibrium geometry the maximum gradient was 10^{-5} Hartree bohr^{-1}.

Results and Discussion

Crystal Structure of the Complex

The structure of the title compound together with the atom-numbering scheme is illustrated in Fig. 1 as refined for room temperature. The packing diagram and the formation of dimers are shown on Fig. 2 (room temperature). Figure 3 shows the chain formation at low temperature.

Room Temperature

There are three independent molecules in the unit cell (Fig. 1). In two of them (molecules A and B), the six-membered rings rotate around the central C–C bond, with

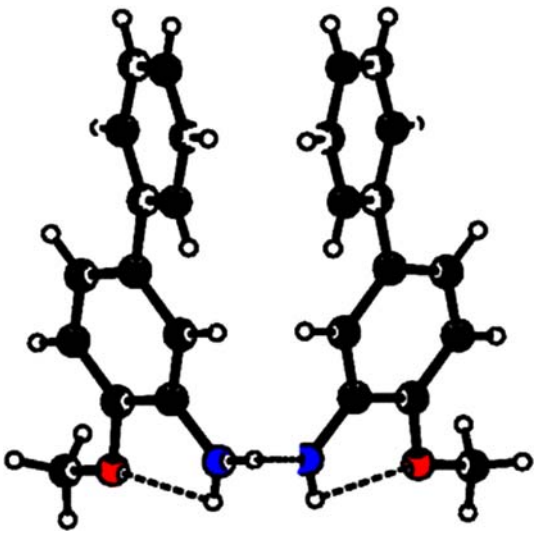

Fig. 2 One of the dimers joined by H-bonds depicted as dashed lines (room temperature data)

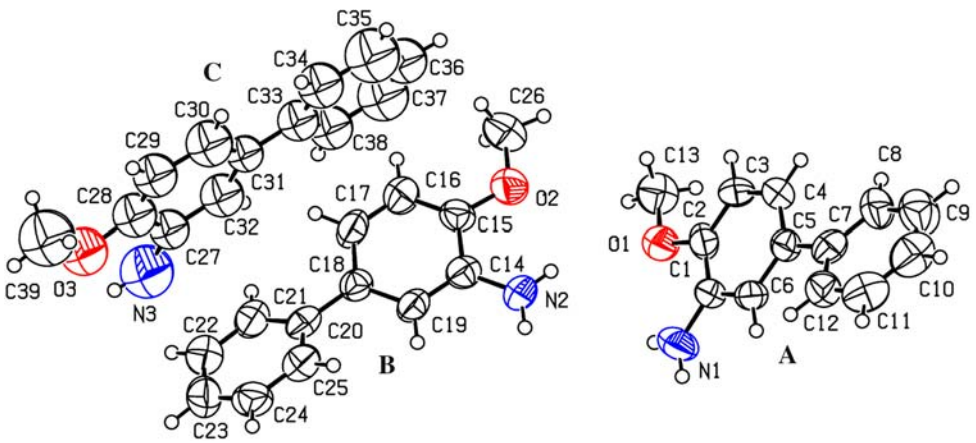

Fig. 1 ORTEP diagram of the title compound with the ellipsoids drawn at the 50% probability level, with the atomic labelling scheme, for room temperature

Table 1 Summary of crystallographic results

Empirical formula	$C_{13}H_{13}NO$	
Formula weight	199.24	
Wavelength (Å)	0.71073	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Z	12	
Calculated density (g/cm^3)	1.227	
Absorption coefficient (mm^{-1})	0.139	
F(000)	1272	
Crystal size (mm)	0.44 × 0.05 × 0.02	
Temperature (K)	293(2)	120(2)
a (Å)	5.9900(2)	5.8336(9)
b (Å)	20.4873(6)	20.443(3)
c (Å)	26.3727(8)	26.077(4)
Volume (Å^3)	3236.43(17)	3109.8(8)
θ range for data collection (°)	1.84–28.39	1.85–27.90
Index ranges	$-8 < h < 7$, $-27 < k < 27$, $-35 < l < 23$	$-7 < h < 7$, $-26 < k < 24$, $-34 < l < 23$
Reflections collected/unique	33667/7890 [R(int) = 0.0882]	14130/4183 [R(int) = 0.0905]
Completeness to $\theta = 27.5°$	98.2%	98.5%
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	4533/0/409	4183/0/409
Goodness-of-fit on F^2	1.163	1.001
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0868$	$R1 = 0.0669$
	$wR2 = 0.2252$	$wR2 = 0.1429$
R indices (all data)	$R1 = 0.2638$	$R1 = 0.1571$
	$wR2 = 0.2982$	$wR2 = 0.1812$
Largest diff. peak and hole (e Å^{-3})	0.365 and −0.334	0.360 and −0.289

angles between the least-squares plane of the two phenyl rings of 24.0(3)° for A and 29.7(3)° for B. In the third molecule (molecule C), all the atoms share approximately the same plane, the angle between the two least-squares plane being 6.9(4)°. Molecules A and B are bonded in dimers through hydrogen bonds (Fig. 2). In A and B, the hydrogen atoms of the amine group are both involved in H-bonding. One of the H atoms is shared intramolecularly with the O atom of the methoxy group. H1A, bonded to N1, is orientated towards the N2 atom of a neighboring molecule joining the A and B molecules in dimers. Molecule C does not establish intermolecular H-bonds with the neighboring molecules and only the intramolecular N-H···O bond is seen. However, an intermolecular interaction of the X–H···π type is seen, since the H3A atom, bonded to N3, is orientated towards the π electron cloud of the C20–C25 ring of a near molecule [N3···ring centroid distance is 3.518(9) Å and angle 137°]. The thermal displacement parameters of the atoms belonging to the C molecule are significantly higher than those of molecules A and B, showing some disorder of this molecule.

Low Temperature

At low temperature the atomic disorder of molecule C is attenuated, but the molecule remains without establishing conventional H-bonds with any of the neighboring molecules. There are more H-bonds between A and B so that not only the dimers formation is observed, but also the dimers are joined together in columns running along the a-axis (Table 3). This is due to the decreasing of intermolecular distance. Figure 3 shows the columns projected along the axis and the N3–H3A···ring_centroid intermolecular interaction that subsists at low temperature. The conformation of the molecules does not change much with the lowering of the temperature (Table 2), the angle between the least-squares planes of the two phenyl ring of each molecule is 23.5(2)° for A, 29.2(2)° for B and 7.1(3)° for C.

DFT Studies

The value of the dihedral angle ϕ(C2C1C1′C2′) (Fig. 4) found in this study for the 2-methoxy-5-phenylaniline

Table 2 Selected bond lengths (Å) and angles (°) as determined by X-ray diffraction

	293(2) K	120(2) K
C5–C7	1.497(9)	1.485(7)
O1–C2	1.385(7)	1.382(6)
O1–C13	1.425(9)	1.430(6)
N1–C1	1.400(7)	1.397(6)
C2–O1–C13	117.0(5)	116.1(4)
C4–C5–C7–C8	−24.4(9)	−23.9(7)
C18–C20	1.479(9)	1.482(7)
O2–C15	1.354(7)	1.369(6)
O2–C26	1.438(9)	1.428(6)
N2–C14	1.387(7)	1.401(6)
C15–O2–C26	115.5(5)	115.9(4)
C17–C18–C20–C21	29.5(9)	29.1(7)
C31–C33	1.428(9)	1.489(8)
O3–C28	1.405(9)	1.391(7)
O3–C39	1.399(13)	1.411(7)
N3–C27	1.412(9)	1.382(7)
C28–O3–C39	112.4(7)	116.0(5)
C30–C31–C33–C34	10.3(11)	8.7(8)

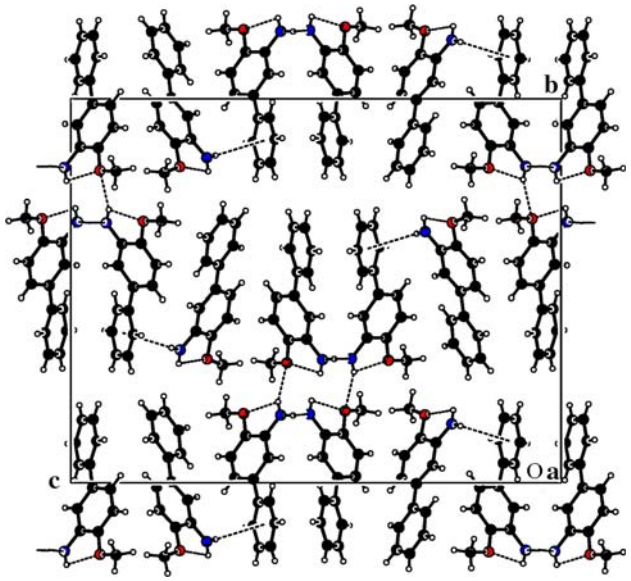

Fig. 3 Column formation at low temperatures by H-bonding shown as dashed lines. A N–H···π interaction is also shown as a dashed line

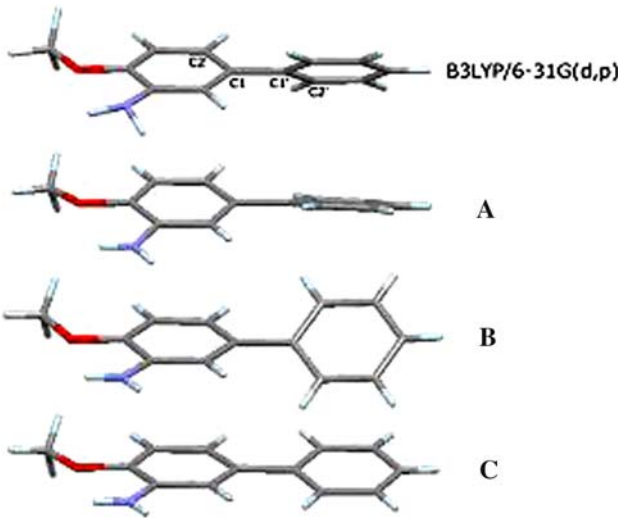

Fig. 4 Comparison of experimental and DFT optimized (B3LYP/6-31G(*d,p*)) structures of 2-methoxy-5-phenylaniline. Dihedral angle Φ (C2C1C1′C2′) between phenyl rings: DFT −38.5°, Molecule A: −23.5(4)°, Molecule B: 28.6(4)°, and Molecule C: 3.7(4)°

molecule in gas phase using DFT at the B3LYP/6-31*G*(*d,p*) level is −38.5°. This value is very close to the torsion angle obtained by other authors using several DFT generalized gradient approximation methods for the biphenyl molecule in gas phase [22], which is 37–41°. In solution a smaller dihedral angle of 19–26° and 32° was estimated for the biphenyl molecule from spectroscopic data [23]. Biphenyl, when influenced by the crystalline environment, exhibits a planar conformation.

The substituted biphenyl molecule, 2-methoxy-5-phenylaniline, retains the same conformation as biphenyl in the gas phase but differs significantly in the crystalline environment. Strong H-bonding arranging the molecules in dimers or columns, result in the decrease of the torsion angle to the range 23–30°. A third molecule, less influenced by conventional hydrogen bonding, crystallizes with the two phenyl rings sharing approximately the same plane. Such flexibility may be used to our advantage as to improve the transport properties of the molecules when polymerized since it has been shown that the phenyl–phenyl tilting angle influence such properties [24].

Table 3 Geometric parameters of hydrogen bond network (K, °, and Å)

T		D–H	H···A	D–H···A	Bond angle
293(2)	N1–H1A···N2^{i}	0.86	2.50	3.321(9)	160
120(2)	N1–H1A···N2^{i}	0.86	2.46	3.256(6)	154
	N2–H2A···N1	0.86	2.57	3.337(6)	150
	N2–H2B···O1	0.86	2.53	3.352(5)	159

Symmetry operator *i*: $-1/2 + x$, $3/2 - y$, $-z$

Supplementary Material

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC 607101. Copies of this information may be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Acknowledgement This work was supported by Fundação para a Ciência e a Tecnologia under project POCI/AMB/55281/2004.

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